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(54) Title: Optical Fiber Cladding Resin Composition

(57) Abstract

CONSTITUTION

Optical fiber cladding resin composition containing radical curable compound obtained by reacting epoxy acrylate and polyisocyanate and compound having terminal polymerizable unsaturated group and hydroxy group; optical fiber cladding resin composition containing, in addition to the radical curable compound, radical curable compound obtained by reacting isocyanuric acid derivative having terminal polymerizable unsaturated group and hydroxy group, polyisocyanate and compound having terminal polymerizable unsaturated group and hydroxy group, or radical polymerizable compound obtained by reacting polyol, polyisocyanate and compound having terminal polymerizable unsaturated group and hydroxy group; optical fiber cladding resin composition further containing polymerizable thinner and/or photosensitizer.

EFFECTS

Provided are optical fiber cladding resin compositions having small curing shrinkage and giving tough cured products with very high rigidity, and the compositions are useful in making ultra-high-density multicore optical fiber cables.

CLAIMS

1. Optical fiber cladding resin composition containing radical curable compound (A) obtained by reacting epoxy acrylate (a1) and polyisocyanate (a2) and compound (a3) having terminal polymerizable unsaturated group and hydroxy group.

2. Optical fiber cladding resin composition according to Claim 1, wherein the epoxy acrylate (a1) has a cyclic chemical structure.

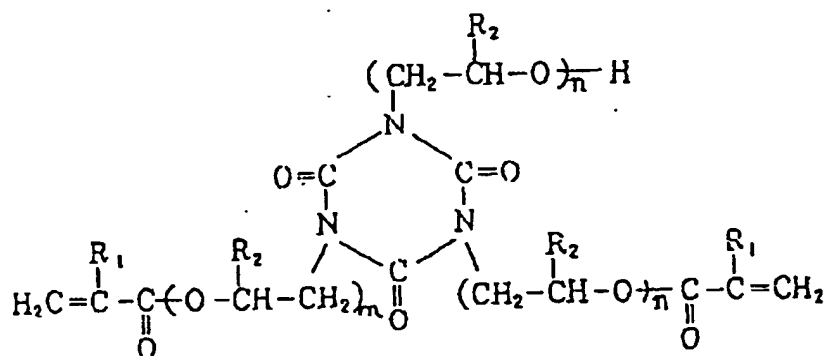
3. Optical fiber cladding resin composition according to Claim 1, wherein the epoxy acrylate (a1) is the reaction product from bisphenol and/or phenol resin glycidyl ether and compound having terminal polymerizable unsaturated group and carboxy group.

4. Optical fiber cladding resin composition according to Claim 1, wherein the polyisocyanate (a2) has cyclic chemical structure.

5. Optical fiber cladding resin composition containing, in addition to the radical curable compound (A) described in Claims 1-4, radical curable compound (B) obtained by reacting isocyanuric acid derivative (b1) having terminal polymerizable unsaturated group and hydroxy group, polyisocyanate (b2) and compound (b3) having terminal polymerizable unsaturated group and hydroxy group.

6. Optical fiber cladding resin composition according to Claim 5, wherein the isocyanuric acid derivative (b1) can be represented by general formula 1:

[Structure 1]



(in the formula, R₁ represents hydrogen atom or methyl group; R₂ represents hydrogen atom or C₁₋₅ alkyl group; n is a whole number of 1-20).

7. Optical fiber cladding resin composition according to Claim 5, wherein the polyisocyanate (b2) is a diisocyanate with molecular weight less than 500.

8. Optical fiber cladding resin composition according to Claim 5, wherein the polyisocyanate (b2) is a trimer of a diisocyanate.

9. Optical fiber cladding resin composition according to Claim 5, wherein the polyisocyanate (b2) is a trimer of diisocyanate containing at least one monomer diisocyanate having cyclic structure.

10. Optical fiber cladding resin composition containing, in addition to the radical curable compounds (A) described in Claims 1-4, a radical curable compound (C) obtained by reacting polyol (c1), polyisocyanate (c2) and compound (c3) having terminal polymerizable unsaturated group and hydroxy group.

11. Optical fiber cladding resin composition according to Claim 10, wherein the polyol (c1) has molecular weight 600-2500.

12. Optical fiber cladding resin composition, characterized by comprising optical fiber cladding resin composition described in any one of Claims 1-11 and also polymerizable thinner (D).

13. Optical fiber cladding resin composition according to Claim 12, wherein the polymerizable thinner (D) is a monofunctional vinyl monomer that can form a homopolymer with glass-transition temperature 60°C or higher.

14. Optical fiber cladding resin composition, characterized by comprising any one of the resin compositions described in Claims 1-11 or 13 and also photosensitizer (E).

15. Optical fiber cladding resin composition, characterized by comprising the resin composition of Claim 12 and also photosensitizer (E).

16. Optical fiber cladding resin composition according to Claim 14 or 15, wherein the photosensitizer (E) contains one or more chosen from the group comprising 1-

hydroxycyclohexyl phenyl ketone, thioxanthone, thioxanthone derivative, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1[sic], 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone-1.

DETAILED EXPLANATION OF THE INVENTION

[0001]

INDUSTRIAL APPLICATION FIELD

The present invention concerns optical fiber cladding resin compositions having extremely high rigidity and small curing shrinkage.

[0002]

CONVENTIONAL TECHNOLOGY

Recently, dramatic technological progress has been made for optical fibers as transmission media for information in large volume and they are being used in practical applications in various fields. Usually, optical fibers are made of glass with outer diameter about 125 μm , and light passes through the glass for information transmission. However, glass easily suffers physical damage by contact with other materials or dust in the atmosphere or chemical corrosion by chemical materials such as moisture, etc. in air, and starting from such damage point, breakage occurs easily. On the other hand, when external stress is exerted to glass optical fibers, loss of the light passing through the glass is high, resulting in problems of inaccurate information transmission. To overcome such problems, usually, optical fibers are imparted a resin coating layer comprising a very soft primary coating layer then highly rigid secondary coating layer.

[0003]

Due to the necessity of forming a resin layer simultaneously with melt drawing of a glass rod at high temperature by drawing-coating process, active energy beam-curable resin compositions that can be cured instantly from liquid to solid by UV or electron beam are used as the resins for such resin coatings. Such active energy beam-curable resin compositions are described in Japanese Kokoku Patent No. Hei 2[1990]-21424, etc.

[0004]

PROBLEMS TO BE SOLVED BY THE INVENTION

However, recently, transmission of information in larger volume has been demanded, and to carry out this, ultra-high-density multicore optical fiber cables with small outer diameter are

needed (1991 Denshiseihotsushingakkaishunkizenkokudaikaikoenronbunshu, Monograph 4, B-871). To realize this, the optical fiber resin coating layer has to be made thinner and the diameter smaller without lowering transmission characteristics. Thus, for active energy beam-curable resin compositions for the secondary coating layer, resin compositions with extremely postcuring high rigidity, low residual stress in the resin coating layer in the drawing-coating process and small curing shrinkage are sought (1991 Denshiseihotsushingakkaishunkizenkokudaikaikoenronbunshu, Monograph 4, B-543).

[0005]

However, with the active energy-curable resin compositions shown in Japanese Kokoku Patent No. Hei 2[1990]-2142, resin coating layers with high rigidity exceeding 120 kg/mm^2 cannot be obtained, and the curing shrinkage is large. Namely, in the field of optical fiber cladding resin compositions, developing active energy beam-curable resin compositions giving tough cured products with extremely high rigidity and small curing shrinkage is a task.

[0006]

MEANS FOR SOLVING THE PROBLEMS

Under such circumstances, as a result of an intense investigation, we have discovered that radical polymerizable compounds obtained by reacting compounds having certain chemical structure give optical fiber cladding resin compositions giving tough cured products with extremely high rigidity and small curing shrinkage. Thus, the present invention is attained.

[0007]

CONSTITUTION

The present invention concerns optical fiber cladding resin compositions with extremely high rigidity and small curing shrinkage. Namely, the present invention concerns optical fiber cladding resin compositions containing radical curable compound (A) obtained by reacting epoxy acrylate (a1) and polyisocyanate (a2) and compound (a3) having terminal polymerizable unsaturated group and hydroxy group and optical fiber cladding resin compositions characterized by containing radical curable compound (A) wherein the epoxy acrylate (a1) has a cyclic structure.

[0008]

Optical fiber cladding resin compositions characterized by containing radical curable compound (A), wherein the epoxy acrylate (a1) is the reaction product from bisphenol and/or phenol resin glycidyl ether and compound having terminal polymerizable unsaturated group and

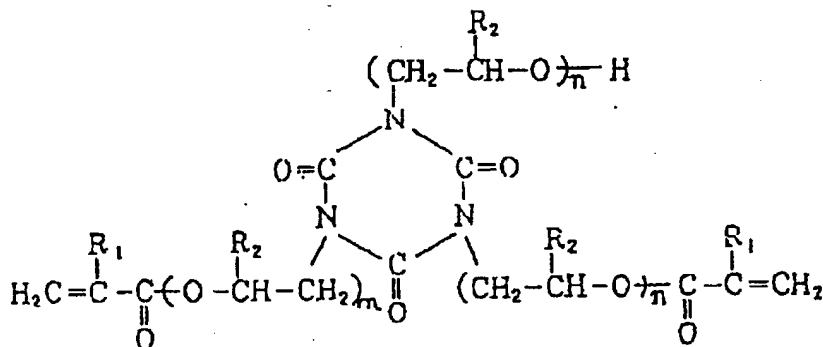
carboxy group. Optical fiber cladding resin compositions characterized by containing radical curable compound (A) wherein the polyisocyanate (a2) has cyclic chemical structure.

[0009]

Optical fiber cladding resin composition containing, in addition to the radical curable compound (A) radical curable compound (B) obtained by reacting isocyanuric acid derivative (b1) having terminal polymerizable unsaturated group and hydroxy group, polyisocyanate (b2) and compound (b3) having terminal polymerizable unsaturated group and hydroxy group. Optical fiber cladding resin compositions, wherein the isocyanuric acid derivative (b1) can be represented by general formula 1:

[0010]

[Structure 2]



(in the formula, R_1 represents hydrogen atom or methyl group; R_2 represents hydrogen atom or C_{1-5} alkyl group; n is a whole number of 1-20).

[0011]

Optical fiber cladding resin compositions, wherein the polyisocyanate (b2) is a diisocyanate with molecular weight less than 500. Optical fiber cladding resin composition, wherein the polyisocyanate (b2) is a trimer of a diisocyanate. Optical fiber cladding resin composition, wherein the polyisocyanate (b2) is a trimer of diisocyanate containing at least one monomer diisocyanate having cyclic structure. Optical fiber cladding resin composition containing, in addition to the radical curable compounds (A), a radical curable compound (C) obtained by reacting polyol (c1), polyisocyanate (c2) and compound (c3) having terminal polymerizable unsaturated group and hydroxy group.

[0012]

Optical fiber cladding resin compositions, wherein the polyol (c1) has molecular weight 600-2500. Optical fiber cladding resin composition is characterized by comprising the above optical fiber cladding resin composition and also polymerizable thinner (D). In the optical fiber cladding resin composition, the polymerizable thinner (D) is a monofunctional vinyl monomer that can form a homopolymer with glass-transition temperature 60°C or higher. The optical fiber cladding resin composition is characterized by comprising any one of the above resin compositions and also photosensitizer (E).

[0013]

Optical fiber cladding resin compositions, wherein the photosensitizer (E) contains one or more chosen from the group comprising 1-hydroxycyclohexyl phenyl ketone, thioxanthone, thioxanthone derivative, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1[sic], 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone-1.

[0014]

Next, the present invention is explained in further detail. The epoxy acrylate (a1) used in the synthesis of the radical polymerizable compound (A) of the present invention is any reaction product from glycidyl group-containing compound and compound having terminal polymerizable unsaturated group and carboxy group, while preferred for the high rigidity of cured products are reaction products from glycidyl compounds having cyclic structure such as benzene ring, naphthalene ring, spiro ring, dicyclopentadiene, tricyclodecane, etc. and compounds having terminal polymerizable unsaturated group and carboxy group such as acrylic acid, methacrylic acid, etc.

[0015]

Of them, especially preferred for high glass-transition temperature, high rigidity are reaction products from (meth)acrylic acid and glycidyl ethers of aromatic ring-containing phenols such as phenolic resins and bisphenols such as bisphenol A, bisphenol S, bisphenol F, etc. Next, the polyisocyanates (a2) used in the present invention are, e.g. polyisocyanates such as tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, hydrogenated 4,4'-diphenylmethane diisocyanate, xylylene diisocyanate, hydrogenated xylylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, 1,5-naphthalene diisocyanate, toluidine diisocyanate, p-phenylene diisocyanate, trans-cyclohexane 1,4-diisocyanate, lysine diisocyanate, tetramethylxylene diisocyanate, lysine ester triisocyanate, 1,6,11-undecane triisocyanate, 1,8-

diisocyanato-4-isocyanatomethyloctane, 1,3,6-hexamethylene triisocyanate, bicycloheptane triisocyanate, trimethylhexamethylene diisocyanate, etc.

[0016]

Of these, polyisocyanates with cyclic structure are especially preferred for obtaining high rigidity. Next, the compounds (a3) having terminal polymerizable unsaturated group and hydroxy group are, e.g., 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, 2-(meth)acryloyloxyethyl 2-hydroxyethyl phthalate, pentaerythritol tri(meth)acrylate, 3-acryloyloxyglycerin mono(meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-1-(meth)acryloyloxy-3-(meth)acryloyloxypropane, glycerin di(meth)acrylate, polypropylene glycol mono(meth)acrylate, polyethylene glycol mono(meth)acrylate, poly- ϵ -caprolactone mono(meth)acrylate, 4-hydroxybutyl (meth)acrylate, ϵ -caprolactone mono(meth)acrylate, etc.

[0017]

The ratio of (a1), (a2) and (a3) used in the radical curable compound (A) of the present invention is given below. Namely, with the total number of hydroxy groups of (a1) being 1, total number of isocyanate groups of the compound (a2) being m and the total number of hydroxy groups of the compound (a3) being n, $(1 + n)/m = 0.5-10.0$, preferably $0.8-5.0$, $1/n = 0.2-6.0$, preferably $0.2-3.0$. Such radical curable compounds (A) are useful as, even alone, optical fiber cladding resin compositions.

[0018]

For further improving curability, the present invention also provides optical fiber cladding resin compositions containing, in addition to the radical curable compound (A), radical curable compound (B) obtained by reacting isocyanuric acid derivative (b1) having terminal polymerizable unsaturated group and hydroxy group, polyisocyanate (b2) and compound (b3) having terminal polymerizable unsaturated group and hydroxy group.

[0019]

Namely, the isocyanuric acid derivatives (b1) having terminal polymerizable unsaturated group and hydroxy group used for the synthesis of the radical polymerizable compound (B) may be any compound having polymerizable unsaturated group, hydroxy group and isocyanuric acid structure in the molecule, while commonly used are products obtained by addition of isocyanuric acid with lactones such as γ -butyrolactone, γ -valerolactone, δ -valerolactone, ϵ -caprolactone, D-glucono-1,4-lactone, 1,10-phenanthrenecarbolactone, 4-penten-5-olide, 12-dodecanolide, etc.,

alkylene oxide such as ethylene oxide, propylene oxide, etc., or cyclic ether such as tetrahydrofuran, etc., followed by dehydrative condensation or ester exchange reaction with carboxy compound having polymerizable unsaturated group such as (meth)acrylic acid, (meth)acrylic acid esters, etc. at an equivalent ratio, leaving 1 mol or more of the hydroxy group formed.

[0020]

Of these, the radical curable compounds of isocyanuric acid derivative represented by the general formula 1 are preferred for making optical fiber cladding resin compositions for tough resin coating layer with high rigidity. For polyisocyanates (b2), polyisocyanates similar to the above (a2) are used. Of these, polyisocyanates with molecular weight 500 or lower are preferred for obtaining high rigidity. Furthermore, besides those described above, the polyisocyanates (b2) used in the present invention may be trimers of the above diisocyanates. The diisocyanate trimers are compounds having isocyanuric acid skeleton formed by trimerization of diisocyanate and three isocyanate groups. The three diisocyanates used as the monomers may be same or different.

[0021]

Of these, for high glass-transition temperature, the diisocyanate trimers from at least one diisocyanate monomer having aromatic or alicyclic ring structure are preferred. The (b3) used in the present invention may be similar to the above (a3), e.g., 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, 2-(meth)acryloyloxyethyl 2-hydroxyethyl phthalate, pentaerythritol tri(meth)acrylate, 3-acryloyloxyglycerin mono(meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-1-(meth)acryloyloxy-3-(meth)acryloyloxypropane, glycerin di(meth)acrylate, polypropylene glycol mono(meth)acrylate, polyethylene glycol mono(meth)acrylate, poly- ϵ -caprolactone mono(meth)acrylate, 4-hydroxybutyl (meth)acrylate, ϵ -caprolactone mono(meth)acrylate, etc.

[0022]

The ratio of (b1), (b2) and (b3) used in the radical curable compound (A) of the present invention is given below. Namely, with the total number of hydroxy groups of (b1) being 0, total number of isocyanate groups of the compound (b2) being p and the total number of hydroxy groups of the compound (b3) being q, $(o + q)/p = 0.5-2.0$, preferably $0.8-1.5$, $q/o = 0-8.0$, preferably $0-4.0$.

[0023]

The radical curable compounds (B) may contain both isocyanuric acid derivative (b1)-the above isocyanate reaction product and the isocyanuric acid derivative (b1)-diisocyanate trimer reaction product. For such radical curable compounds (B), to 100 parts of the radical curable compound (A), 300 parts of the radical curable compound (B) is the upper limit. Besides the above (A), the optical fiber cladding resin compositions of the present invention may contain radical curable compound (C) synthesized from conventional polyol (c1), polyisocyanate (c2) and compound (c3) having terminal polymerizable unsaturated group and hydroxy group.

[0024]

The above polyols (c1) may be polyester polyols obtained by polycondensation of polybasic acids and polyhydroxy alcohols, polyester polyols obtained by ring-opening polymerization of lactones, polyether polyols that are cyclic ether polymers and copolymers of two or more of alkylene oxides such as ethylene oxide, propylene oxide, butylene oxide, etc., tetrahydrofuran, alkyl-substituted tetrahydrofuran, etc. Of these, radical curable compounds (C) using polyols of molecular weight 400-3000 are preferred, and of these, radical curable compounds (C) using polyols of molecular weight 600-2500 are especially preferred for obtaining optical fiber cladding resin compositions with high rigidity and low viscosity. The polyisocyanates (c2) may be similar to the polyisocyanates (a2), and the compounds (c3) having terminal polymerizable unsaturated group and hydroxy group may be similar to those (a3) having terminal polymerizable unsaturated group and hydroxy group.

[0025]

The ratio of (c1), (c2) and (c3) used in the radical curable compound (A) of the present invention is given below. Namely, with the total number of hydroxy groups of (c1) being r , total number of isocyanate group of the compound (c2) being s and the total number of hydroxy groups of the compound (c3) being t , $(r + t)/s = 0.5-10.0$, preferably $0.8-5.0$, $r/t = 0.2-6.0$, preferably $0.2-3.0$. Such radical curable compounds (C) are usually used in 400 parts as the upper limit to 100 parts of the radical curable compound (A), while the range of 25-150 parts is preferred for obtaining high rigidity and strength and toughness.

[0026]

In addition to the radical curable compounds (A), for reduced viscosity, the optical fiber cladding resin compositions of the present invention may contain polymerizable thinners (D). The polymerizable thinners (D) are compounds having amino group and hydroxy group, to which (meth)acrylic acid is bonded by esterification reaction, e.g., monofunctional

polymerizable thinners such as methoxyethylene glycol (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, β -(meth)acryloyloxyethyl hydrogen phthalate, β -(meth)acryloyloxyethyl hydrogen succinate, nonylphenoxyethyl (meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate, phenoxyethyl (meth)acrylate, phenoxypolyethylene glycol (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, β -(meth)acryloyloxypropyl hydrogen phthalate, β -(meth)acryloyloxypropyl hydrogen succinate, butoxypolyethylene glycol (meth)acrylate, alkyl (meth)acrylate, cyclohexyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, isobornyl (meth)acrylate, benzyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate,

[0027]

2-hydroxypropyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, 2-(meth)acryloyloxyethyl 2-hydroxyethyl phthalate, 3-acryloyloxyglycerin mono(meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-1-(meth)acryloyloxy-3-(meth)acryloyloxypropane, polypropylene glycol mono(meth)acrylate, polyethylene glycol mono(meth)acrylate, poly- ϵ -caprolactone mono(meth)acrylate, dialkylaminoethyl (meth)acrylate, glycidyl (meth)acrylate, mono[2-(meth)acryloyloxyethyl] acid phosphate, trichloroethyl (meth)acrylate, 2,2,3,3-tetrachloropropyl (meth)acrylate, 2,2,3,4,4,4-hexafluorobutyl (meth)acrylate, perfluorooctylethyl (meth)acrylate, dicyclopentenylalkyl (meth)acrylate, dicyclopentenyl (meth)acrylate,

[0028]

tricyclodecanyl (meth)acrylate, tricyclodecanyloxyethyl (meth)acrylate, isobornyloxyethyl (meth)acrylate, morpholine (meth)acrylate, N-vinylpyrrolidone, N-vinylpyridine, N-vinylcaprolactone, etc.; bifunctional polymerizable thinners such as 2,2-dimethyl-3-hydroxypropyl 2,2-dimethyl-3-hydroxypropionate di(meth)acrylate, ethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, propylene glycol (meth)acrylate, polypropylene glycol di(meth)acrylate,

[0029]

1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, glycerin di(meth)acrylate, neopentyl glycol di(meth)acrylate, neopentyl glycol hydroxypivalate di(meth)acrylate, bisphenol A-ethylene oxide adduct di(meth)acrylate, bisphenol A-propylene oxide adduct di(meth)acrylate, 2,2'-di(hydroxypropoxyphenyl)propane di(meth)acrylate, 2,2'-di(hydroxyethoxyphenyl)propane di(meth)acrylate, tricyclodecanedimethylol di(meth)acrylate, 2,2'-di(glycidyoxyphenyl)propane (meth)acrylate, etc.;

[0030]

polyfunctional polymerizable thinners such as trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, tetramethylolmethane tri(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, tris(2-hydroxyethyl) isocyanurate tri(meth)acrylate, tris(hydroxypropyl) isocyanurate tri(meth)acrylate, trimellitic acid tri(meth)acrylate[sic], triallyl trimellitate, triallyl isocyanurate, etc.

[0031]

Of these, especially preferred are monofunctional vinyl monomers such as dicyclopentenyl (meth)acrylate, tricyclodecanyl (meth)acrylate, bornyl (meth)acrylate, isobornyl (meth)acrylate, N-vinyl-2-pyrrolidone, N-vinylpyridine, morpholine (meth)acrylate, N-vinylcaprolactone[sic], vinylcarbazole, etc. for homopolymer glass-transition temperature 60°C or above and low viscosity without sacrifice of glass-transition temperature and strength and toughness. The amount of the polymerizable thinners (D) used should be 5-60 wt% of radical curable compound + polymerizable thinner, preferably 12-45 wt%.

[0032]

Usually, in the case of curing the optical fiber cladding resin compositions of the present invention by UV radiation, it is preferred to add photosensitizers (E) such as photopolymerization initiators, etc. to the above (A), (B), (C) and (D) components. Such photosensitizers may be, e.g., 4-dimethylaminobenzoic acid, 4-dimethylaminobenzoic acid esters, alkoxyacetophenones, benzil dimethyl ketal, benzophenone, benzophenone derivatives, alkyl benzoylbenzoates, bis(4-dialkylaminophenyl) ketone, benzil and benzil derivatives, benzoin and benzoin derivatives, benzoin alkyl ethers, 2-hydroxy-2-methylpropiophenone, 1-hydroxycyclohexyl phenyl ketone, thioxanthone, thioxanthone derivatives, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1[sic], 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone-1, etc.

[0033]

Of these, for high curability, especially preferred photosensitizers (E) are one or more chosen from the group comprising 1-hydroxycyclohexyl phenyl ketone, thioxanthone and its derivatives, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1 [sic], 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone-1.

[0034]

The photosensitizers (E) are added for curing the optical fiber cladding resin compositions of the present invention by UV radiation, and their content is usually 0.2-10 wt% to 100 wt% for the total of the radical curable compounds (A), (B) and (C) and the polymerizable thinners (D), while 0.05-5 wt% is especially preferred for high curability.

[0035]

Next, the content of the radical curable compound (A) in the optical fiber cladding resin compositions of the present invention is 5-100 wt% to 100 wt% for the total of the radical curable compounds (B) and (C) and the polymerizable thinners (D), while 10-80 wt% is preferred for low viscosity, excellent moldability and strength and toughness of the cured products. While the radical curable compound (B) is not essential in the optical fiber cladding resin compositions of the present invention, it is added for improved curability and strength and toughness. The polymerizable thinners (D) are added for lowering the viscosity of the optical fiber cladding resin compositions of the present invention as needed, and their content is usually 5-60 wt% to 100 wt% for the total of the radical curable compound (A), radical curable compound (B) and (C) and polymerizable thinners (D), while 12-45 wt% is especially preferred for low viscosity, excellent moldability and strength and toughness of the cured products.

[0036]

Beside the above components, the optical fiber cladding resin compositions of the present invention may also contain polymerization inhibitors such as hydroquinone, methoquinone, etc., hindered phenol antioxidants, hindered amine yellowing preventers, phosphate ester type decolorizers, defoamers such as silicone oils, etc., release agents, leveling agents, etc. The cured products from the optical fiber cladding resin compositions of the present invention should have rigidity modulus 120 kg/mm^2 or above with small curing shrinkage, thus suitable for optical fiber cladding resin compositions, useful in ultra-high-density multicore optical fiber cables.

[0037]

EXAMPLES

Next, the present invention is explained in further detail with Application Examples, Comparative Examples, and manufacturing examples. However, the present invention is not limited to such examples. In the examples, parts and % are always based on weight.

[0038]

MANUFACTURING EXAMPLE 1

In a flask fitted with a stirrer, thermometer and reflux condenser, 222 parts of isophorone diisocyanate were stirred and heated to 70°C, treated dropwise over a period of 1 h with 336 parts of hydroxy group-containing acrylate compound (hydroxy group value 167 mg-KOH/g) obtained by ring opening of ϵ -caprolactone with hydroxyethyl acrylate to obtain an intermediate compound I-1. Next, in a flask fitted with a stirrer, thermometer and reflux condenser, 376 parts of bisphenol A epoxy resin (epoxy equivalent 188 g/eq) and 144 parts of acrylic acid at 100°C for 8 h, treated with 558 parts of the intermediate compound I-1 and reacted at 80°C for 5 h to obtain a radical curable compound (A-1).

[0039]

MANUFACTURING EXAMPLE 2

In a flask fitted with a stirrer, thermometer and reflux condenser, 222 parts of isophorone diisocyanate were stirred and heated to 70°C, treated dropwise over a period of 1 h with 116 parts of hydroxyethyl acrylate to obtain an intermediate compound I-2. Next, in a flask fitted with a stirrer, thermometer and reflux condenser, 376 parts of bisphenol A epoxy resin (epoxy equivalent 188 g/eq) and 144 parts of acrylic acid at 100°C for 8 h, treated with 338 parts of the intermediate compound I-2 and reacted at 80°C for 5 h to obtain a radical curable compound (A-2).

[0040]

MANUFACTURING EXAMPLE 3

In a flask fitted with a stirrer, thermometer and reflux condenser, 72 parts of acrylic acid was added to 269 parts of isobornyl acrylate and 218 parts of phenol type epoxy resin (epoxy equivalent 218 g/eq), heated at 100°C for 1 h for the reaction, treated with 338 parts of the intermediate compound I-2 and heated at 80°C for 5 h to obtain a radical curable compound (A-3).

[0041]

MANUFACTURING EXAMPLE 4

In a flask fitted with a stirrer, thermometer and reflux condenser, 456 parts of trishydroxyethyl isocyanurate acrylic acid ester (hydroxy group value 123 mg-KPH/g) and 84 parts of hexamethylene diisocyanate were stirred at 80°C for 5 h to obtain a radical curable compound (B-1).

[0042]

MANUFACTURING EXAMPLE 5

In a flask fitted with a stirrer, thermometer and reflux condenser, 456 parts of trishydroxyethyl isocyanurate acrylic acid ester (hydroxy group value 123 mg-KPH/g) and 672 parts of hydroxy group-containing acrylate compound (hydroxy group value 167 mg-KOH/g) obtained by ring opening of ϵ -caprolactone with hydroxyethyl acrylate were heated under stirring to 80°C, treated with 550 parts of polyisocyanate compound (22.9 NCO%) that is a trimer obtained by isocyanuration of hexamethylene diisocyanate and stirred and heated at 80°C for 5 h to obtain a radical curable compound (B-2).

[0043]

MANUFACTURING EXAMPLE 6

In a flask fitted with a stirrer, thermometer and reflux condenser, 444 parts of isophorone diisocyanate was heated to 70°C, treated with 1000 parts of polytetramethylene glycol (hydroxy group value 112 mg-KOH/g), heated at 70°C for 5 h, treated with 232 parts of hydroxyethyl acrylate and reacted for 5 h to obtain a radical curable compound (C-1).

[0044]

MANUFACTURING EXAMPLE 7

In a flask fitted with a stirrer, thermometer and reflux condenser, 352 parts of tolylene diisocyanate were heated to 70°C, treated with 2000 parts of polyether polyol (hydroxy group value 56 mg-KOH/g) obtained by copolymerizing tetrahydrofuran and propylene oxide, reacted at 70°C for 5 h, treated 232 parts of hydroxyethyl acrylate, and further reacted for 5 h to obtain a radical curable compound (C-2).

[0045]

MANUFACTURING EXAMPLE 8

A mixture formed by adding 44 parts of acrylic acid to 376 parts of epoxy resin (epoxy equivalent 188 g/eq) obtained by reacting epichlorohydrin and bisphenol A was reacted at 100°C for 8 h to obtain a radical curable compound (Y).

[0046]

APPLICATION EXAMPLES 1-8, COMPARATIVE EXAMPLES 1 AND 2

The radical curable compounds (A-1)~(A-3), (B-1), (B-2), (C-1), (C-2), (Y) synthesized in the above Manufacturing Examples 1-8, polymerizable thinners (D-1)~(D-4) and photosensitizers (E-1)~(E-6) were compounded in the ratio shown in the table into a uniform

mixture, filtered through a 10 μm cartridge filter to obtain optical fiber cladding resin compositions of the present invention and comparison. Next, the optical fiber cladding resin compositions were measured for ① viscosity, ② rigidity modulus of cured product, and ③ curing shrinkage according to the methods described below.

① Viscosity

Measured at 25°C using a Brookfield rotating viscometer.

Preparation of cured sheet

Each optical fiber cladding resin composition was coated using an applicator on a clean smooth glass plate and irradiated using a metal halide lamp conveyer type UV irradiator under a nitrogen atmosphere at UV dose 1000 mj/cm^2 to obtain a cured sheet.

[0047]

PREPARATION OF MEASUREMENT SHEET

The above cured sheet was punched using the super dumbbell (JIS K7113-2 dumbbell) of the Dumbbell Co. and measured for rigidity modulus. The cured sheet had a thickness in the range of 0.03-0.06 mm. To prevent slip of the measurement sheet in the chuck during measurement, four places left and right and up and down outside the bench marks (25 mm) were fixed by iron plate with thickness 0.3 mm and length and width 20 mm and an adhesive (Aron Alpha, product of Toa Gosei Kagaku Co.).

[0048]

② Rigidity modulus of cured product

Using RTM-100 tensile tester of Toyo Baldwin Co., the air chuck gap of the tensile tester was set at 25 mm, and the fixed part of the measurement sheet was set in the chuck gap. The specimen was then stretched at a rate of 1 mm/min, measuring the stress at the time of 2.5% elongation, and the rigidity modulus was calculated using the equation: rigidity modulus = stress at 2.5% elongation/0.025. Measurements were made three times and the average value is given.

[0049]

③ Curing shrinkage

Each optical fiber cladding resin composition shown in the table was added to a height of about 5 mm in a stainless pan with inner diameter 30 mm and height 10 mm and irradiated with UV radiation of 1000 mj/cm^2 in a nitrogen atmosphere using a metal halide lamp conveyer type UV irradiator to obtain a cured specimen for density measurement, which was then measured for density (Ds) at $23 \pm 2^\circ\text{C}$. The immersion liquid used was 99.5% ethanol. The optical fiber cladding resin compositions of the table were also measured for density (DL) at $23^\circ\text{C} \pm 2^\circ\text{C}$

according to JIS K6901. Measurements were made twice, and the curing shrinkage was calculated using the equation: curing shrinkage = $(D_s - DL)/D_s$

[0050]

EXPLANATION OF THE COMPONENTS IN THE EXAMPLES IN TABLES

The polymerizable thinners (D) and photosensitizers (E) in the tables are described below.

- D-1: isobornyl acrylate
- D-2: N-vinyl-2-pyrrolidone
- D-3: pentaerythritol triacrylate
- D-4: tetraethylene glycol diacrylate

[0051]

- E-1: 1-hydroxycyclohexyl phenyl ketone
- E-2: 2,4,6-trimethylbenzoyldiphenylphosphine oxide
- E-3: 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone-1
- E-4: 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1[sic]
- E-5: 2,4-diethylthioxanthone
- E-6: diethoxyacetophenone

[0052]

Table I

Items		Application Example 1	Application Example 2
Compositions	Radical curable compound (A)	(A-1)	72.5
		(A-2)	-
		(A-3)	-
	Radical curable compound (B)	(B-1)	-
		(B-2)	-
	Radical curable compound (C)	(C-1)	-
		(C-2)	-
	Radical curable compound (Y)		-
	Polymerizable thinner (D)	(D-1)	17.5
		(D-2)	10.0
		(D-3)	-
		(D-4)	-
	Photosensitizer (E)	(E-1)	-
		(E-2)	3.0
		(E-3)	0.5
		(E-4)	-
		(E-5)	-
		(E-6)	-
Properties	Viscosity (poise/25°C)		91
	Rigidity modulus (kg/mm ²)		508
	Curing shrinkage (%)		5.1

[0053]

Table II

Items			Application Example 3	Application Example 4
Compositions	Radical curable compound (A)	(A-1)	-	40.0
		(A-2)	-	-
		(A-3)	50.0	-
	Radical curable compound (B)	(B-1)	-	22.8
		(B-2)	-	9.7
	Radical curable compound (C)	(C-1)	-	-
		(C-2)	-	-
	Radical curable compound (Y)		-	-
	Polymerizable thinner (D)	(D-1)	25.0	17.5
		(D-2)	25.0	10.0
		(D-3)	-	-
		(D-4)	-	-
	Photosensitizer (E)	(E-1)	-	-
		(E-2)	2.0	-
		(E-3)	-	-
		(E-4)	-	1.0
		(E-5)	-	0.2
		(E-6)	-	-
Properties	Viscosity (poise/25°C)		325	69
	Rigidity modulus (kg/mm ²)		243	207
	Curing shrinkage (%)		5.5	5.3

[0054]

Table III

Items			Application Example 5	Application Example 6
Compositions	Radical curable compound (A)	(A-1)	20.0	36.5
		(A-2)	-	-
		(A-3)	-	-
	Radical curable compound (B)	(B-1)	26.3	-
		(B-2)	26.2	-
	Radical curable compound (C)	(C-1)	-	36.5
		(C-2)	-	-
	Radical curable compound (Y)		-	-
	Polymerizable thinner (D)	(D-1)	17.5	12.0
		(D-2)	10.0	15.0
		(D-3)	-	-
		(D-4)	-	-
	Photosensitizer (E)	(E-1)	-	4.0
		(E-2)	1.0	-
		(E-3)	-	-
		(E-4)	-	-
		(E-5)	-	-
		(E-6)	-	-
Properties	Viscosity (poise/25°C)		64	41
	Rigidity modulus (kg/mm ²)		214	124
	Curing shrinkage (%)		5.6	4.5

[0055]

Table IV

Items		Application Example 7
Compositions	Radical curable compound (A)	(A-1)
		(A-2)
		(A-3)
	Radical curable compound (B)	(B-1)
		(B-2)
	Radical curable compound (C)	(C-1)
		(C-2)
	Radical curable compound (Y)	
	Polymerizable thinner (D)	(D-1)
		(D-2)
		(D-3)
		(D-4)
	Photosensitizer (E)	(E-1)
		(E-2)
		(E-3)
		(E-4)
		(E-5)
		(E-6)
Properties	Viscosity (poise/25°C)	
	Rigidity modulus (kg/mm ²)	
	Curing shrinkage (%)	

[0056]

Table V

Items			Comparative Example 1	Comparative Example 2
Compositions	Radical curable compound (A)	(A-1)	-	-
		(A-2)	-	-
		(A-3)	-	-
	Radical curable compound (B)	(B-1)	-	-
		(B-2)	-	-
	Radical curable compound (C)	(C-1)	60.0	30.0
		(C-2)	-	-
	Radical curable compound (Y)		10.0	22.0
	Polymerizable thinner (D)	(D-1)	10.0	3.0
		(D-2)	10.0	3.0
		(D-3)	5.0	14.0
		(D-4)	5.0	28.0
	Photosensitizer (E)	(E-1)	-	-
		(E-2)	-	-
		(E-3)	-	-
		(E-4)	-	-
		(E-5)	-	-
		(E-6)	3.0	3.0
Properties	Viscosity (poise/25°C)		29.5	11.5
	Rigidity modulus (Kg/mm ²)		55	111
	Curing shrinkage (%)		9.5	7.5

[0057]

EFFECTS OF THE INVENTION

According to the present invention, active energy beam-curable resin compositions with low curing shrinkage and giving cured products with extremely high rigidity and strength and toughness can be obtained, thus these resin compositions can be used for making ultra-high-density multicore optical fiber cables.



TRANSLATIONS

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